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(54) Prevention of plant damage by environmental hazards.

(57) A method for the prevention or reduction of damage to vegetation by acidic and other toxic contamination in the atmosphere comprises applying to the vegetation a coating agent that acts as a protective unidirectionally permeable membrane allowing the vegetation to breathe but not to absorb contaminants that are either gaseous or that are dissolved in atmospheric water.

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PREVENTION OF PLANT DAMAGE BY ENVIRONMENTAL HAZARDS

This invention is concerned with the prevention of plant damage by environmental hazards. So-called "acid rain" has received wide publicity over the past few years, and the counteraction of the effect on plants of acid materials in the atmosphere and of the effect of ultraviolet light, particularly in cases where one effect accentuates the other, is both ecologically sound and environmentally desirable.

U.K. Patent No. GB 2 030 452-B discloses and claims a method of applying certain plant-growth regulators in conjunction with a smaller amount of an additive that occurs naturally in the cells of living organisms and that modifies the metabolism of plants. In order to enhance the effect of the plant-growth regulator, the additive being applied not more than 15 days before or after the plant-growth regulator, in which the additive is glucose, hydrolysed starch, sucrose, fructose, glycerol, glyceraldehyde, erythrose, ribulose, xylulose or arabinose or an ester or glycoside or metabolic equivalent of such a carbohydrate, an acid of the Krebs Tricarboxylic Acid Cycle or a metabolic precursor thereof, a vitamin or coenzyme, a purine or pyrimidine nucleoside or nucleotide or a precursor thereof, a naturally occurring fat or oil, or an amino acid. Compositions containing the two ingredients are also disclosed and claimed. Insecticides, nematicides, fungicides and herbicides may also be applied in conjunction with the additive in order to enhance their effect.

U.K. Patent No. GB-2 063 235-B discloses and claims a method for the prevention or reduction of loss of seeds by splitting of seed-bearing bodies of plants, comprising applying to the plants, not more than fifteen days before the crop is ready for harvesting, a coating or layering substance that acts as a semi-permeable membrane allowing water from the seed-bearing bodies to be lost but not substantially reabsorbed. The preferred substance is a mixture containing di-*l*-*p*-menthene and certain of its polymers. Other monoterpenes ( $C_{10}H_{16}$ ) can also be used. The agents can be used in admixture with one another.

Apart from monoterpenes, the following compounds are suitable, though this is not an exhaustive list:-

1. Terpene hydrocarbons of the elementary composition  $C_{15}H_{24}$  (sesquiterpenes)
2. Terpene hydrocarbons of the elementary composition  $C_{20}H_{32}$  (diterpenes)
- 5 3. Terpene hydrocarbons of the elementary composition  $C_{30}H_{48}$  (triterpenes)
4. Terpenes having 40 carbon atoms (tetraterpenes)
5. Bicyclic and tricyclic monoterpenes and their derivatives (e.g. oxygenated derivatives) such as  $\alpha$ -pinene,  $d$ -camphor,  
10  $d$ -borneol,  $d$ -tanacetone,  $\beta$ -thujone,  $d$ - $\Delta^3$ -carene
6. Terpene resins (compounded with or without natural or synthetic rubbers)
7. Gum turpentine
8. Sulphate of turpentine
- 15 9. Wood turpentine
10. Pine oils
11. Terpineols
12. Non-oxidizing Alkyd Resins, e.g. those of the castor oil, coconut oil, hydrogenated castor oil, lauric acid, oil-free, saturated acid and  
20 synthetic fatty acid types
13. Oxidizing Alkyd Resins, e.g. acrylic-resin-modified dehydrated castor oil types, epoxide-resin-modified, isophthalic-acid-based types, linoleic-rich oil type, linseed oil types, linseed oil/dehydrated castor oil types, linseed oil/soya bean oil types, linseed oil/tung oil types,  
25 maleic-resin-modified, marine oil types, phenolic-resin-modified, rosin-modified, safflower seed oil types, silicone-resin-modified, soya bean oil types, soya bean oil/tung oil types, styrenated types, sunflowerseed oil types, tall oil types, tobaccoseed oil types, unmodified types, vinyltoluene-modified types and water-soluble  
30 types
14. Benzoguanamine resins
15. Styrene polymers and copolymers, e.g. polystyrene and styrene/maleic anhydride and butadiene/styrene copolymer resins
16. Carbamide resins
- 35 17. Copal ester resins
18. Coumarone-indene resins

19. Cresylic resins
20. Epoxy resins - e.g. dehydrated castor oil types, linseed oil types, linseed oil/rosin types, phenolic-resin-modified, soya bean oil types, styrenated types, vinyltoluene-modified, and unmodified types as well as those sold under the trade marks Epikote 205, Epikote 825, Epikote 828 and Epikote 1001
21. Epoxide melamine condensates
22. Epoxide phenolic condensates
23. Ester gums
24. Fumaric resins
25. Furan resins
26. Ketone resins
27. Maleic resins
28. Melamine resins - e.g. butylated types, hexamethoxymethyl types and formaldehyde condensates
29. Metallic rosinates - e.g. calcium or zinc resinates, zinc/calcium mixtures both rosin or modified rosin
30. Phenolic resins and modified phenolic resins - e.g. phenol/aldehyde resole condensates adducted to rosin or modified rosin, as well as phenol/formaldehyde resins
31. Phenoxy resins
32. Polybutadiene resins
33. Polybutene resins
34. Polycarbonate resins
35. Polyisobutylene resins
36. Polyester resins - e.g. polyacrylate and polymethacrylate ester resins
37. Polysulphide resins
38. Polyurethane resins - e.g. modified types and oil-modified types
39. Polyvinyl acetal resins
40. Polyether resins - e.g. polyvinyl ether resins
41. Polyvinyl formal resins
42. Rosin derivatives - e.g. esters of rosin, copal, rosin acids or rosin modified by hydrogenation, polymerization isomerization or disproportionation with glycerol, pentaerythritol or other polyhydric alcohols
43. Maleic/fumaric condensate resins - e.g. maleic or fumaric

- acid/anhydride adducts on rosin or modified rosins, their esters with glycerol, pentaerythritol or other polyhydric alcohols
- 44. Silicone resins and polymers
  - 45. Urea resins - e.g. urea-formaldehyde
  - 46. Xylene-formaldehyde resins
  - 47. Natural gums/resins - e.g. accoroides, arabic, benzoin, copals, damar, elemi, gamboge, karaya, mastic, rosin, sandarac, shellac and tragacanth
  - 48. Acrylic polymers and copolymers - e.g. polyacrylic acid, polyacrylamide, polyacrylonitrile, poly(methyl methacrylate) and poly(ethyl acrylate/butyl acrylate)
  - 49. Cellulose ethers - e.g. hydroxyethyl cellulose and sodium carboxymethyl cellulose
  - 50. Cellulose esters - e.g. methyl cellulose
  - 51. Hydrocarbon resins - e.g. petroleum resins
  - 52. Polyamide resins
  - 53. Rubbers - e.g. natural rubber, butyl, rubber, nitrile rubber, polychloroprene, rubber/oil emuline and polyurethane rubber and cyclized rubber resins
  - 54. Vinyl polymers and copolymers other than those already mentioned - e.g. poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl butyral), poly(vinyl pyrrolidone), poly(vinyl acetate/vinyl chloride) and poly(vinyl acetate/acrylate) and
  - 55. Natural drying oils, with or without metal accelerators - e.g. linseed oil and tung oil and mixtures of them.

The present invention is based on the discovery that coating substances of the above type can be used to reduce the damage to vegetation, particularly to the leaves of deciduous and evergreen trees and shrubs, resulting from exposure to toxic gases or particulate toxic material, the deposition on them of rain contaminated by acid, or other toxic contaminants either before or after these contaminants have been affected by ultraviolet light and/or atmospheric ozone. Such contaminants include sulphurous and sulphuric acids, dissolved sulphur dioxide, nitrous and nitric acids, and other toxic gases and particulate matter produced from power stations, industrial plants and the exhaust fumes of cars and other motor vehicles. In the case of trees growing at high elevations the effect of

ultraviolet light and ozone on such gases may be such as to substantially increase their toxic properties to vegetation.

In accordance with the present invention, a method for the prevention or reduction of damage to vegetation by acidic and other toxic contamination in the atmosphere comprises applying to the vegetation a coating agent that may act as a protective preferentially unidirectionally permeable membrane allowing the vegetation to breathe but not to absorb toxic gases or atmospheric water and contaminants dissolved in it. Vegetation that can be protected in accordance with the invention includes trees, shrubs and herbaceous plants.

The substance may be applied during growth or dormancy of the vegetation. During dormancy or other periods of restricted growth the coating material may be used at levels giving a higher degree of protection but giving a much greater reduction in the uptake of carbon dioxide and reduction in transpiration.

The additives disclosed in U. K. Patent GB-2 030 452 B can be used in conjunction with the coating agent in order to encourage resistance to and/or recovery from damage from the atmospheric pollutants mentioned. Such of those additives as are basic in character, for example the amino acids asparagine and glutamine, are of especial value in neutralizing the effects of acidity. Amino acids containing more than one amino group per carboxy group are particularly suitable. Other substances such as calcium or magnesium carbonate or hydroxide and other buffers and alkalis may be used to neutralize acidity and combined in the coating agent, but in the case of calcium compounds care is required in view of the lime-hating nature of certain shrubs.

The coating agent along with the additives described herein may also be used in conjunction with plant hormones (synthetic or natural) to counter senescence and other tissue degradation induced by atmospheric pollution. These may include 1,3-diphenylurea, N-(phenylmethyl)-9-(tetrahydro-2H-pyran-2-yl)-9H-purin-6-amine, extracts of seaweed, and other natural plant extracts containing cytokinin activity. Such preparations may be applied by spraying from the ground but may more usefully be applied by spraying from aircraft.

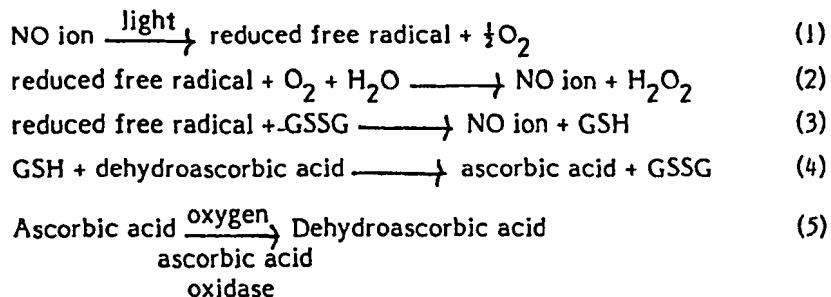
Because of the weakened condition of the vegetation it will be more susceptible to fungal and insect attack. It may therefore be beneficial to include an insecticide and/or fungicide with the coating agent.

The damage caused by such toxic gases or vapours to vegetation exposed to them may be exacerbated where the plant has suffered previous ultraviolet light damage or where initial damage by the said toxic gases or vapours results in damage by ultraviolet light that would otherwise not have taken place or would have been significantly less. Such ultraviolet light damage is likely to be more severe where the vegetation is exposed to high levels of ultraviolet irradiation, e.g. where it is growing at high altitudes.

The coating agents described above, especially those based on pinenene, terpenes and di-*p*-menthene and its polymers act to reduce ultraviolet light and hence may act as a sun-screen or ultraviolet filter to the leaf. This effect may be further enhanced by adding to the coating material or using in its place a chemical known to screen out ultraviolet irradiation. Such chemicals include but are not limited to pine oils, oils of plants such as lemon, olive, coconut and jujuba; substances such as borneol, limonene and terpineol; cinnamic acid, hydroxy-cinnamic acid and benzoic acid and the salts of these acids; and pigments and substances that absorb strongly at wavelengths below 350 Angstroms (35μm).

Free-radical formation from atmosphere pollutants is an additional hazard to plants. Photosynthetic electron flow reduces oxides of nitrogen to form a free radical, and this is converted back to the oxide of nitrogen, with concomitant formation of hydrogen peroxide, by re-oxidation by molecular (atmospheric) oxygen. The hydrogen peroxide is the damaging agent and the reaction producing it can be very rapid, especially in bright sunshine. It can however be slowed by providing an alternative oxidation/reduction system. Thus the use of oxidized glutathione (GSSG) will reoxidize the free radical to the original nitrogen oxide with formation of reduced glutathione (GSH) but no hydrogen peroxide is formed.

One such system is the enzymic re-oxidation of reduced glutathione in conjunction with nicotine adenine dinucleotide phosphate (NADP), which may be stimulated by the use of an NADP precursor such as nicotinamide or nicotinic acid, and a further system is that of ascorbic acid/dehydroascorbic acid catalysed by the enzyme ascorbic acid oxidase, which may be stimulated by the use of ascorbic acid. Ascorbic acid is initially added and converted in the plant to dehydroascorbic acid (5) below. The reactions that take place with NO and GSSG are thus:



Thus the formation of hydrogen peroxide is slowed down and reaction (2) can be eliminated almost completely by using sufficient amounts of the GSSG and ascorbic acid.

The following Example shows how coniferous trees may be protected  
for toxic acidic atmospheric pollutants by application of a coating in  
accordance with the invention.

## EXAMPLE

15       Eight plants of each of the species sitka spruce (Picea sitchensis),  
Norway spruce (Picea abies) and red spruce (Picea rubens), were divided  
randomly into two groups. Half the plants of each species were coated  
using a mixture containing: water (1790 g), di-1-p-menthene (180 g) and  
alkyl phenol ethylene oxide condensate (30 g). Three days after coating, all  
24 plants were placed in a single fumigation chamber in which the coated  
and uncoated plants were grown for two weeks in eight-hour days at photon  
flux densities of 250  $\mu\text{mole E. m}^{-2} \text{ s}^{-1}$  P.A.R. with temperatures of  
20       18 °C/10 °C day/night. After one week the plants were exposed for 8 hours  
to 8 ppm  $\text{SO}_2$  for one light period and this exposure was repeated one week  
later.

## Results

25 No visible injury occurred to the plants after the first day of  
exposure but needle blemishes developed gradually over the four days after  
the second exposure. The percentages of needles showing injury of any  
degree were counted. Four days after the second exposure at 8 ppm SO<sub>2</sub>  
the mean numbers of needles damaged  $\pm$  standard errors on the coated and  
30 uncoated plants were as follows:

sitka spruce:	uncoated = $1.75 \pm 0.96\%$	coated = $0.25 \pm 0.50\%$
red spruce:	uncoated = $70 \pm 3.5\%$	coated = $2.25 \pm 0.50\%$
Norway spruce:	uncoated = $85 \pm 2.4\%$	coated = $2.75 \pm 1.26\%$

These results indicate that damage is substantially reduced by application of a coating in accordance with the invention.

CLAIMS

1. A method for the prevention or reduction of damage to vegetation by acidic and other toxic contamination in the atmosphere that comprises applying to the vegetation a coating agent that acts as a protective membrane restricting the uptake of contaminants that are either gaseous or that are dissolved in atmospheric water.
2. A method as claimed in Claim 1 in which the coating agent is applied in conjunction with an additive that occurs naturally in the cells of living organisms and that modifies the metabolism of plants.
3. A method as claimed in Claim 1 or 2 in which the coating agent is applied in conjunction with a basic substance.
4. A method as claimed in Claim 3 in which the basic substance is an amino acid, calcium or magnesium carbonate or calcium or magnesium hydroxide or a buffer substance or alkali.
5. A method as claimed in any preceding claim in which the coating agent is applied in conjunction with a natural or synthetic plant hormone.
6. A method as claimed in any preceding claim in which the coating agent is applied in conjunction with a fungicide and/or insecticide.
7. A method as claimed in any preceding claim in which the coating agent is applied in conjunction with a chemical known to screen out ultraviolet radiation.
8. A method as claimed in Claim 7 in which the chemical is a pine oil, lemon oil, olive oil, coconut oil, jujuba oil, borneol, limonene, terpineol, cinnamic or hydroxycinnamic or benzoic acid or a salt thereof, or a pigment that absorbs strongly at wavelengths below 35  $\mu\text{m}$ .
9. A modification of a method as claimed in Claim 7 or 8 in which the said chemical replaces the coating agent.

10. A coating agent that acts as a protective preferentially unidirectionally permeable membrane allowing vegetation to breathe but not to absorb atmospheric water and contaminants dissolved in it or gaseous toxic materials, for use in applying to vegetation to prevent or reduce damage to it by acidic and other toxic atmospheric contamination.

11. A coating agent that acts as a barrier to the uptake by vegetation of atmospheric gases both toxic and non-toxic for use in applying to vegetation during periods of restricted growth as for instance during winter months to prevent or reduce damage to it by acidic and other toxic atmospheric contamination.



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EUROPEAN SEARCH REPORT

0169663

Application number

EP 85 30 4408

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
X	EP-A-0 044 224 (M.J.SAMPSON)  * The whole document *  ---	1-5,8-11	A 01 N 61/00 A 01 N 3/00
X	CHEMICAL ABSTRACTS, vol. 93, no. 13, 29th September 1980, page 184, no. 126991n, Columbus, Ohio, US; H.HONDA: "Effects of plant covering materials in reducing the air pollution damage of the plants" & KANKYO KAGAKU KENKYU HOKOKU (CHIBA DAIGAKU) 1977-1978 (PUB. 1979). 4, 48-54 * Abstract * ---	1,10, 11	
D,X	EP-A-0 027 344 (N.HUTCHINGS et al.) * Page 2, line 6 - page 5, line 20; page 7, line 25 - page 8, line 12; page 9, lines 17-19 * ---	1,6,8-11	TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	AU-B- 60 281 (C.F.DEZONG et al.)(1980)  * Page 5, line 27 - page 6, line 19; page 8, lines 8-17; page 11, line 4 - page 12, line 5; page 12, lines 17-24; claims * -----	1,3,4, 6-8,10 ,11	A 01 N
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	27-09-1985	FLETCHER A.S.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone	Y : particularly relevant if combined with another document of the same category		
A : technological background	O : non-written disclosure		
P : intermediate document			